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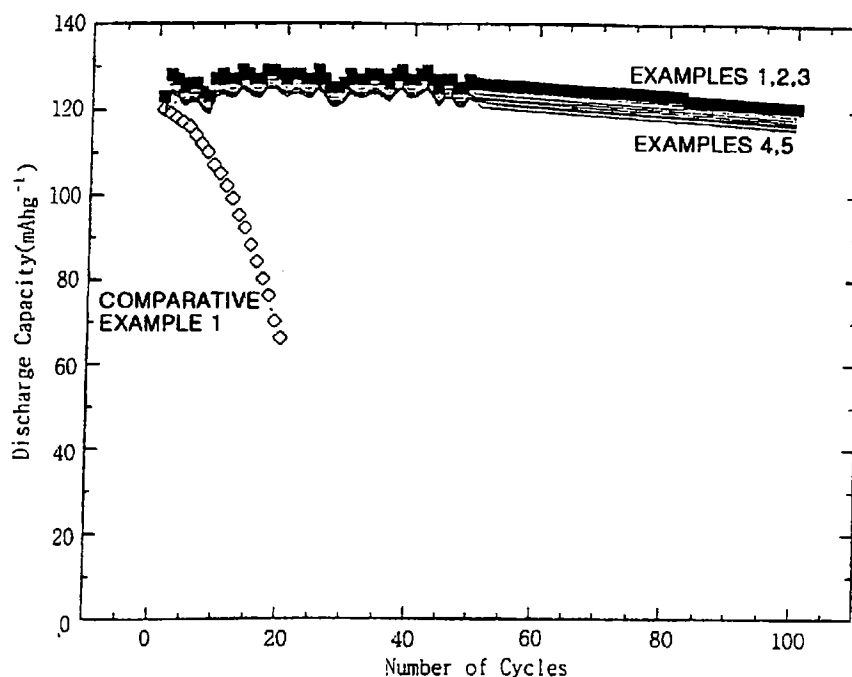
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(54) Title: A LITHIUM ELECTRODE DISPERSED IN POROUS 3-DIMENSIONAL CURRENT COLLECTOR, ITS FABRICATION METHOD AND LITHIUM BATTERY COMPRISING THE SAME



(57) Abstract: The present invention relates to a lithium electrode, its fabrication method, and lithium battery comprising the same, wherein the lithium electrode comprises lithium or lithium alloy dispersed in a porous 3-dimensional current collector.



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**A LITHIUM ELECTRODE DISPERSED IN POROUS 3-DIMENSIONAL  
CURRENT COLLECTOR, ITS FABRICATION METHOD AND LITHIUM  
BATTERY COMPRISING THE SAME**

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**TECHNICAL FIELD**

The present invention relates to a lithium electrode using a porous 3-dimensional current collector, its fabrication method and a lithium battery comprising the same. In particular, the present invention relates to a lithium electrode in which lithium or a lithium alloy is dispersed in pores of a porous 3-dimensional current collector, its fabrication method and a lithium battery comprising the same.

**BACKGROUND ART**

Lithium batteries are generally divided into lithium primary batteries and lithium secondary batteries according to whether or not they can be recharged. In the case of lithium primary batteries, lithium is used as an anode material, and  $\text{Li-MnO}_2$ ,  $\text{Li}(\text{CF})_n$ ,  $\text{Li-SOCl}_2$ , etc. are used as a cathode material according to the type of cathode. These batteries are presently commercialized. (J. O. Basenhard, Handbook of Battery Materials, Wiley-VCH, Weinheim (1999)). However, the lithium primary batteries are disadvantageous in that non-uniform potential distribution occurs due to local dissolution of a lithium electrode, resulting in degradation in the utilization of the electrode.

Meanwhile, in the case of lithium secondary batteries, although

batteries using an anode made of a carbon group material and a cathode made of  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  are presently commercialized, many studies of lithium anodes for increasing the energy density of cells have been made. (D. Linden, Handbook of Batteries, McGraw-Hill Inc., New York (1995)).

5           Although a lithium electrode has a very high theoretical capacity of 3,860 mAh/g, it has a low charge and discharge efficiency, and dendrites are deposited on the surface of the lithium electrode during charging. The deposited dendrites cause an internal short-circuit, so there is a possibility of explosion. Recently, there have been attempts to solve these problems by  
10       means of studies for increasing the charge and discharge efficiency by changing the form of lithium deposition by adding an additive to an electrolyte solution, studies for mixing fine metallic particles such as Ni and Cu, and studies for changing a lithium alloy composition (Handbook 103 of the 35<sup>th</sup> Forum for Discussion on Batteries (1994), Handbook 103 of the 35<sup>th</sup> Forum  
15       for Discussion on Batteries (1994), J.O. Basenhard, Handbook of Battery Materials, Wiley-VCH, Weinheim (1999)). However, no particular solution has been suggested yet.

### **SUMMARY OF THE INVENTION**

20           Therefore, an object of the present invention is to provide a lithium electrode by which the utilization and cycle life of the electrode are increased and the high-rate charge and discharge characteristics are improved.

          Another object of the present invention is to provide a novel lithium electrode in which lithium or a lithium alloy is dispersed in pores of a porous

current collector.

Still another object of the present invention is to provide a fabrication method of the above lithium electrode.

Still another object of the present invention is to provide a lithium  
5 battery comprising the above lithium electrode.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a cross-sectional view showing a lithium electrode according to the present invention.

10 Figure 2 is a graph showing test results of electrode capacities and cycle performance of the lithium batteries obtained in Examples 1 - 5 of the present invention and obtained in Comparative Example 1.

Figure 3 is a graph showing test results of high-rate discharge characteristics of the lithium secondary batteries obtained in Example 1 and  
15 Comparative Example 1.

Figure 4 is a graph showing test results of high-rate discharge characteristics of the lithium primary batteries obtained in Example 6 of the present invention and obtained in Comparative Example 2.

### **DETAILED DESCRIPTION OF THE INVENTION**

20 The present invention will now be described in detail with reference to accompanying drawings.

The present invention relates to an lithium electrode using a porous 3-dimensional current collector, its fabrication method and a lithium battery

using the same. Lithium or a lithium alloy is uniformly filled into pores of the current collector with a method of an electroplating, a melting, a thin film fabrication technique or a particle paste packing, and then optionally pressed, to obtain the lithium electrode in which lithium or a lithium alloy is uniformly dispersed into the pores of 3-dimensional current collector. The present invention can provide a lithium electrode by which a conductivity of the lithium electrode can be increased and potential distribution on the surface of the electrode can be maintained constant, and accordingly, the utilization of lithium and the cycle life can be increased and the high-rate charge/discharge characteristics can be improved.

The present invention will be described in more detail. Figure 1 is a cross-sectional view showing the lithium electrode 100 of the present invention. The Lithium or lithium alloy 101 is uniformly distributed in the pores of the porous current collector 102. Examples of a material of the porous current collector which can be used may include Ni, Cu, Ti, V, Cr, Mn, Fe, Co, Zn, Mo, W, Ag, Au, Ru, Pt, Ir, Al, Sn, Bi, Si, Sb and alloys thereof, but not limited thereto on condition that it is capable of maintaining porosity. Another metal besides the lithium or lithium alloy 101 can be further included in the porous current collector, and examples may include Ni, Cu, Ti, V, Cr, Mn, Fe, Co, Zn, Mo, W, Ag, Au, Ru, Pt, Ir, Al, Sn, Bi, Si, Sb and alloys thereof.

The fabrication method of the lithium electrode of the present invention will be described in more detail. Lithium or lithium alloy is uniformly filled into the pores of a porous current collector with an electroplating, melting or thin film fabrication technique, or lithium particles are uniformly filled into the pores

of a current collector with a paste casting method. Herein, the term "thin film fabrication technique" means a technique to deposit physically under an anhydrous atmosphere. Examples of such thin film fabrication technique include a thermal deposition, electron beam deposition, ion beam deposition, sputtering, arc deposition and laser ablation. In casting method, a paste of lithium or a lithium alloy with a solvent is made and then cast, or lithium or a lithium alloy, a binder such as PVdF and a solvent are mixed in order to form a paste and then cast. Also, if it is necessary, pressing can be carried out to obtain a lithium electrode having a high density. Herein, the term "pressing" means that an application of pressure to make a material have a high density. Means for pressing may include a roll press and a plate press. It is preferred that the pressure applied is usually in the range of 10 kg/cm<sup>2</sup> - 100 ton/cm<sup>2</sup>.

When lithium or a lithium alloy is cast, another metal may be formed simultaneously. Examples of such metal may include Ni, Cu, Ti, V, Cr, Mn, Fe, Co, Zn, Mo, W, Ag, Au, Ru, Pt, Ir, Al, Sn, Bi, Si, Sb or alloys thereof.

The present invention has advantages that the desired metal or alloy can be freely coated or filled into the pores of the porous 3-dimensional current collector, pure lithium and/or metal composite can be coated or filled without an outer contamination, and the composition of lithium-metal, homogeneity of coating, coating thickness and coating time can be controlled by adjusting the coating speed.

In addition, the conductivity of the electrode of the present invention is improved to make the current and potential distribution constant, and thereby, a partial overcharge reaction can be prevented. Accordingly, the

utilization and the cycle life of the electrode are increased, the moving rate of the lithium is not decreased because the electrode layer is porous, and such effect is enlarged in large batteries.

The lithium electrode of the present invention can be used for  
5 fabricating various lithium batteries including lithium primary and secondary batteries. For example, a lithium primary battery can be made using the lithium electrode of the present invention and  $\text{MnO}_2$ ,  $(\text{CF})_n$  or  $\text{SOCl}_2$  as a cathode, and a lithium secondary battery can also be made using the lithium electrode of the present invention and  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  
10  $\text{V}_2\text{O}_5$  or  $\text{V}_6\text{O}_{13}$  as a cathode. Also, it is advantageous in that the lithium electrode of the present invention can be used as an anode of lithium ion batteries using polypropylene, polyethylene or the like as a separator film, lithium polymer batteries using polymer electrolyte and complete solid type lithium batteries using solid electrolyte among the lithium secondary batteries.

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## EXAMPLES

The preparation of the lithium electrode and lithium batteries using the same and advantages of the lithium batteries will now be described in more detail by way of the following examples, to which the present invention is not  
20 limited.

### Example 1

A lithium electrode was fabricated by coating lithium at a thickness of  $20\mu\text{m}$  with an electroplating method into the pores of a porous copper current

collector which was fabricated by an electroplating method. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of acetylene black (AB) and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and then  
5 drying and rolling the obtained plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

#### Example 2

10 A lithium electrode was fabricated by coating lithium at a thickness of  $20\mu\text{m}$  with an electroplating method into the pores of a porous 3-dimensional nickel current collector which was fabricated by an electroplating method. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an  
15 aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

#### 20 Example 3

A lithium electrode was fabricated by making a paste after mixing lithium particles of a few  $\mu\text{m}$  with a solution of a binder PVdF in NMP, packing by casting the paste onto a porous 3-dimensional silver current collector



fabricated by an electroplating method and then drying and rolling the resulting current collector. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

#### 10            Example 4

A lithium electrode was fabricated by coating lithium at a thickness of  $20\mu\text{m}$  with a vacuum deposition method into the pores of a porous 3-dimensional copper current collector which was fabricated by an electroless plating method. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

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#### Example 5

A lithium electrode was fabricated by coating lithium at a thickness of  $20\mu\text{m}$  with a melting method into the pores of a porous 3-dimensional copper

current collector which was fabricated by an electroplating method. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

#### Example 6

A lithium electrode was fabricated by coating lithium at a thickness of  $20\mu\text{m}$  with an electroplating method into the pores of a porous 3-dimensional copper current collector which was fabricated by an electroplating method. A cathode was obtained by adding 5.7g of  $\text{MnO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium battery.

#### Comparative Example 1

A lithium anode was fabricated by pressing a lithium thin plate of  $100\mu\text{m}$  to be  $80\mu\text{m}$  onto an extended copper thin plate. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture

of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a secondary lithium battery.

#### Comparative Example 2

A lithium anode was fabricated by pressing a lithium thin plate at a thickness of  $50\mu\text{m}$  onto a copper thin plate. A cathode was obtained by adding 5.7g of  $\text{LiCoO}_2$ , 0.6g of AB and 0.4g of PVdF to a mixture of NMP and acetone, casting the obtained mixture onto an aluminum thin plate when an appropriate viscosity was obtained, and drying and rolling the resulting plate. The lithium electrode, a PP separator and the cathode were stacked sequentially, and then 1M  $\text{LiPF}_6$  solution in PC/EMC was injected thereto, thereby to fabricate a lithium primary battery.

#### Example 7

Electrode capacities and cycle life characteristics of the lithium secondary batteries obtained in Examples 1 - 5 and in Comparative Example 1 were measured (at a charge/discharge rate  $C/2$ ), and the results are shown in Figure 2. As shown in Figure 2, the lithium batteries comprising the lithium electrode of the present invention exhibited stable discharge capacities regardless the repeated charging/discharging. In addition, the lithium batteries of the present invention exhibited improved cycle life characteristics.

### Example 8

High-rate discharge characteristics of the lithium secondary batteries obtained in Example 1 and Comparative Example 1 were measured, and the results are shown in Figure 3. As shown in Figure 3, the lithium battery comprising the lithium electrode of the present invention was remarkably superior in high-rate discharge characteristic to that of the lithium battery obtained in Comparative Example 1.

### 10 Example 9

High-rate discharge characteristics of the lithium primary batteries obtained in Example 6 and Comparative Example 2 were measured (Figure 4). The results shows that the lithium primary battery comprising the lithium electrode of the present invention was remarkably superior in discharge characteristic to that of the conventional lithium primary battery obtained in Comparative Example 2.

**CLAIMS**

1. A lithium electrode comprising a porous 3-dimensional current collector and lithium or a lithium alloy which is dispersed into the pores of the porous 3-dimensional current collector.
- 5 2. The lithium electrode according to claim 1, wherein a material of the porous current collector is selected from the group consisting of Ni, Cu, Ti, V, Cr, Mn, Fe, Co, Zn, Mo, W, Ag, Au, Ru, Pt, Ir, Al, Sn, Bi, Si, Sb and alloys thereof.
- 10 3. The lithium electrode according to claim 1, wherein the lithium alloy is an alloy of lithium with a metal selected from the group consisting of Al, Sn, Bi, Si, Sb, B and alloys thereof.
- 15 4. The lithium electrode according to claim 1, further comprising a metal in the pores of the porous 3-dimensional current collector.
5. The lithium electrode according to claim 4, wherein the metal is selected from the group consisting of Ni, Cu, Ti, V, Cr, Mn, Fe, Co, Zn, Mo, 20 W, Ag, Au, Ru, Pt, Ir, Al, Sn, Bi, Si, Sb and alloys thereof.
6. A fabrication method of a lithium electrode according to claim 1, comprising a step of uniformly distributing lithium or a lithium alloy and a metal in a porous 3-dimensional current collector with a method selected from the

group consisting of an electroplating, melting, thin film fabrication technique and a paste casting.

7. The method according to claim 6, further comprising a step of pressing.

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8. The method according to claim 7, wherein the pressing is performed by applying a pressure of  $10\text{kg/cm}^2$  -  $100\text{ton/cm}^2$  with a roll press or a plate press.

10 9. The method according to claim 6, wherein the thin film fabrication technique is selected from the group consisting of thermal deposition, electron beam deposition, ion beam deposition, sputtering, arc deposition and laser ablation deposition.

15 10. The method according to claim 6, wherein the paste casting method comprises casting a paste made with lithium or lithium alloy particles and a solvent, or obtained by mixing lithium or lithium alloy particles, a binder and a solvent.

20 11. A lithium battery comprising a cathode, an anode and an electrolyte, wherein the anode is the lithium electrode according to claim 1.

12. The lithium battery according to claim 11, wherein the cathode is selected from the group consisting of  $\text{MnO}_2$ ,  $(\text{CF})_n$  and  $\text{SOCl}_2$ .

13. The lithium battery according to claim 11, wherein the cathode is selected from the group consisting of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$  and  $\text{V}_6\text{O}_{13}$ .

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FIG. 1

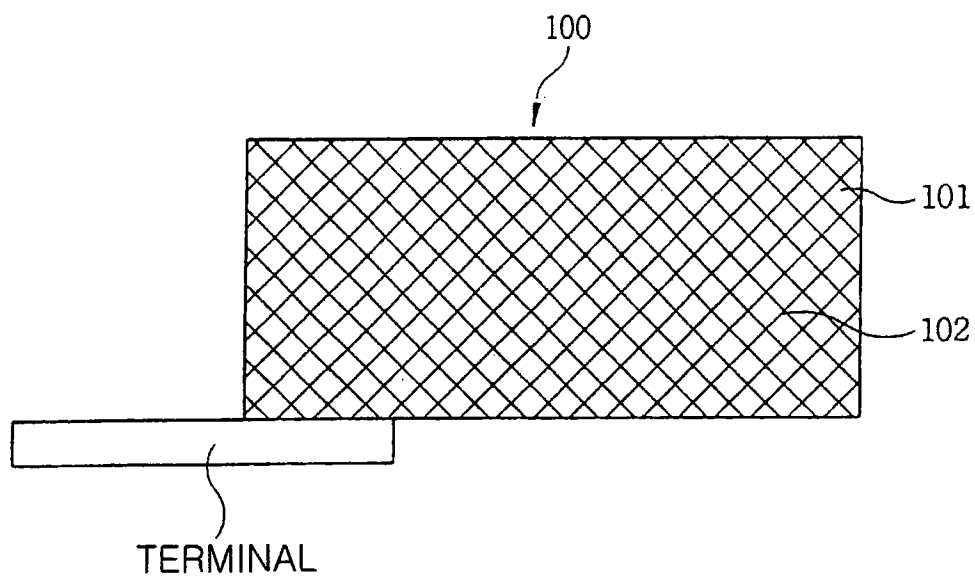




FIG. 2

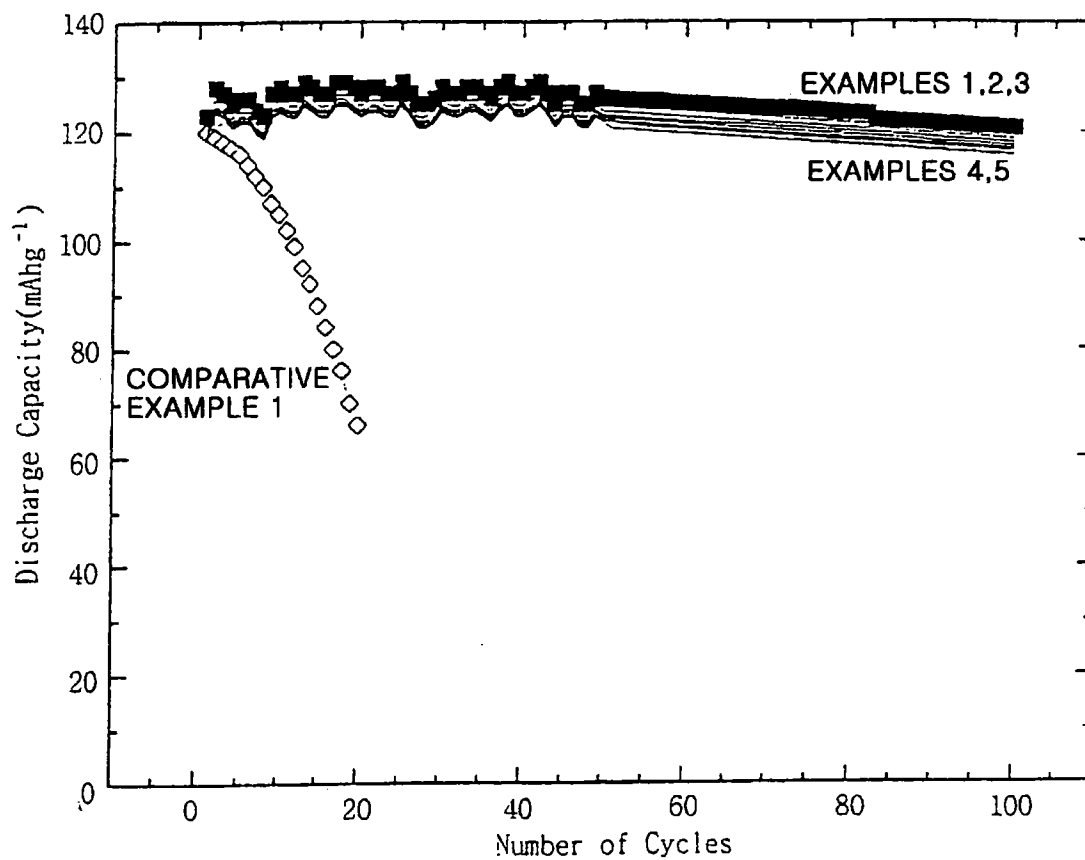


FIG. 3

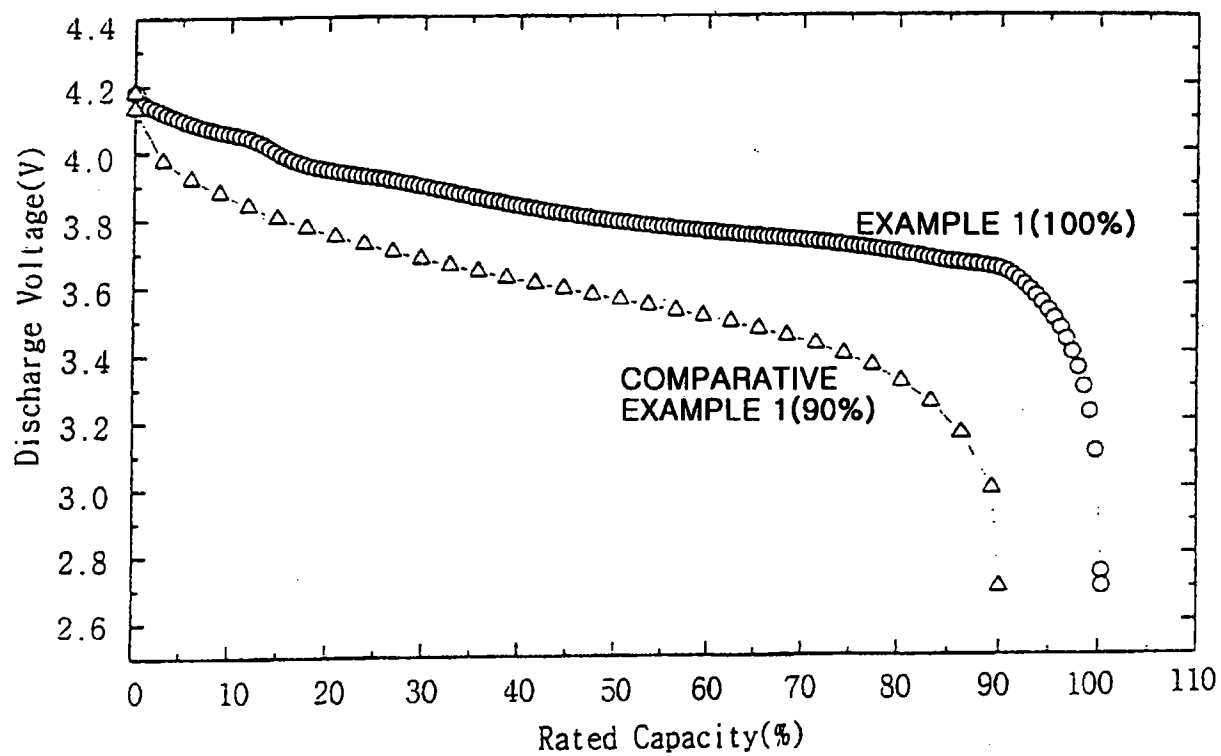
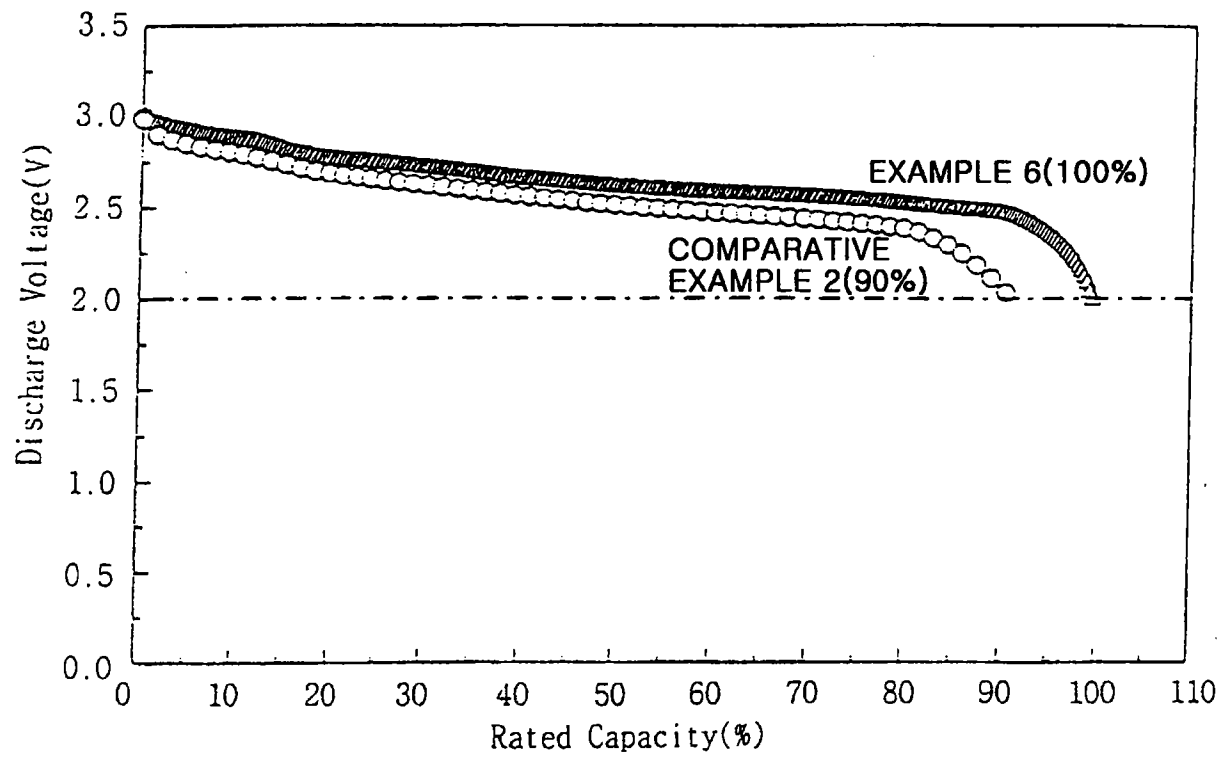


FIG. 4



## INTERNATIONAL SEARCH REPORT

International application No.

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**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 H01M 4/38**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC H01M 4/02, H01M8/02, H01M 4/80

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean patents and applications for inventions since 1975

Korean Utility models and application for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 07-176301A (RICOH CO.LTD) 14.JULY.1995 See the entire document	1-15
A	JP 07-14593A ((FUJIKURA LTD) 17.JANUARY.1995 See the whole document	1-15
A	JP 11-111304A (JAPAN METALS & CHEM CO.LTD) 23.APRIL.1999 See the claims	1-15

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